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UNIVERSITY OF ILLINOIS BULLETIN
ISSUED WEEKLY
Vol. XXII October 20, 1924 No. 8
[Entered as second-class matter December 11, 1912, at the post office at Urbana, Illinois, under the Act of August 24, 1912. Acceptance for mailing at the special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 31, 1918.]

THE ANALYSIS OF FUEL GAS

BY
S. W. PARR
AND
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ENGINEERING EXPERIMENT STATION

Circular No. 12 October, 1924

THE ANALYSIS OF FUEL GAS

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ENGINEERING EXPERIMENT STATION
Published by the University of Illinois, Urbana

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THE ANALYSIS OF FUEL GAS

I. Introduction

1. *Introduction.*—All of the many industries engaged in producing fuel or utilizing it in any way find that gas analysis is an essential accompaniment to their work. In the operation of gas producers, the percentage of carbon monoxide, carbon dioxide, oxygen, hydrogen, and hydrocarbons must be determined. The same determinations must be made for by-product coke oven gas, retort gas, water gas, carburetted water gas, and natural gas. When gas is sold to consumers a very complete check on the composition of the gas is necessary. The analysis must be made rapidly and accurately for it is used in controlling many industrial operations, and determining their efficiency, as well as to indicate to the consumer what he is buying.

II. Outline of Procedure for Fuel Gas Analysis

2. *Outline of Analysis.*—A comprehensive review of the methods employed in gas analysis embodying also investigational work as to the efficiencies of these methods has been made; these details have been included in the appendix. There is here given a synopsis only of the methods which are best adapted to the type of apparatus developed as a result of studies made in connection with this work. These methods are listed in the order of procedure necessary for carrying out the analysis. A discussion of alternative methods or methods to be used with other forms of apparatus is given fully in the appendix.

Outline of Procedure for Complete Analysis of a Fuel Gas

Constituent	Reagent Employed	Remarks
Carbon dioxide CO_2	Sodium hydroxide NaOH	Where the absorption is to be made in a closed pipette, potassium hydroxide is preferred. See appendix.
Ethylene C_2H_4 Benzene C_6H_6 Heavy Hydrocarbons or Illuminants	Bromine water	For alternative use of fuming sulphuric acid or separation of illuminants, see appendix.

Outline of Procedure for Complete Analysis of a Fuel Gas (Continued)

Oxygen O_2	Alkaline pyrogallate	
Carbon monoxide CO	Acid or ammoniacal cuprous chloride	For conditions where combustion to CO_2 may be applied, etc., see appendix.
Hydrogen H_2	Oxidation by CuO at 300° C.	This replaces the usual explosion or palladium absorption method.
Methane, Ethane C_nH_{2n+2}	Slow combustion over red hot platinum in oxygen	
Nitrogen N_2	By difference	

III. Apparatus for Fuel Gas Analysis

3. *Modified Form of Orsat Apparatus.*—As a result of the various studies carried on in this laboratory in connection with water gas reactions, the cracking of oils and tars, and the carbonization of coal, there has been developed an apparatus suitable for the scientific study of gas mixtures, which, because of the rapidity as well as the accuracy of operation, is especially well adapted to commercial and control purposes. The earlier form of this apparatus, shown in Fig. 1, is here reproduced because by means of it the evolution of the final instrument as shown in Fig. 2 may be more readily understood.

The assembly of a number of individual gas pipettes of the Hempel type for a special purpose, as in the ordinary Orsat apparatus for flue gas analysis, is familiar to everyone and does not need illustration. The Orsat apparatus is usually limited to the three common constituents of flue gases, and is not suitable for the analysis of a fuel gas. However, in Fig. 1 there is shown an apparatus consisting of an assembly of all of the Orsat parts with additions which make it applicable to a range sufficient to cover combustible gases as well. For this reason, therefore, it may be conveniently referred to as an enlarged or modified Orsat. In this apparatus the pipettes used for

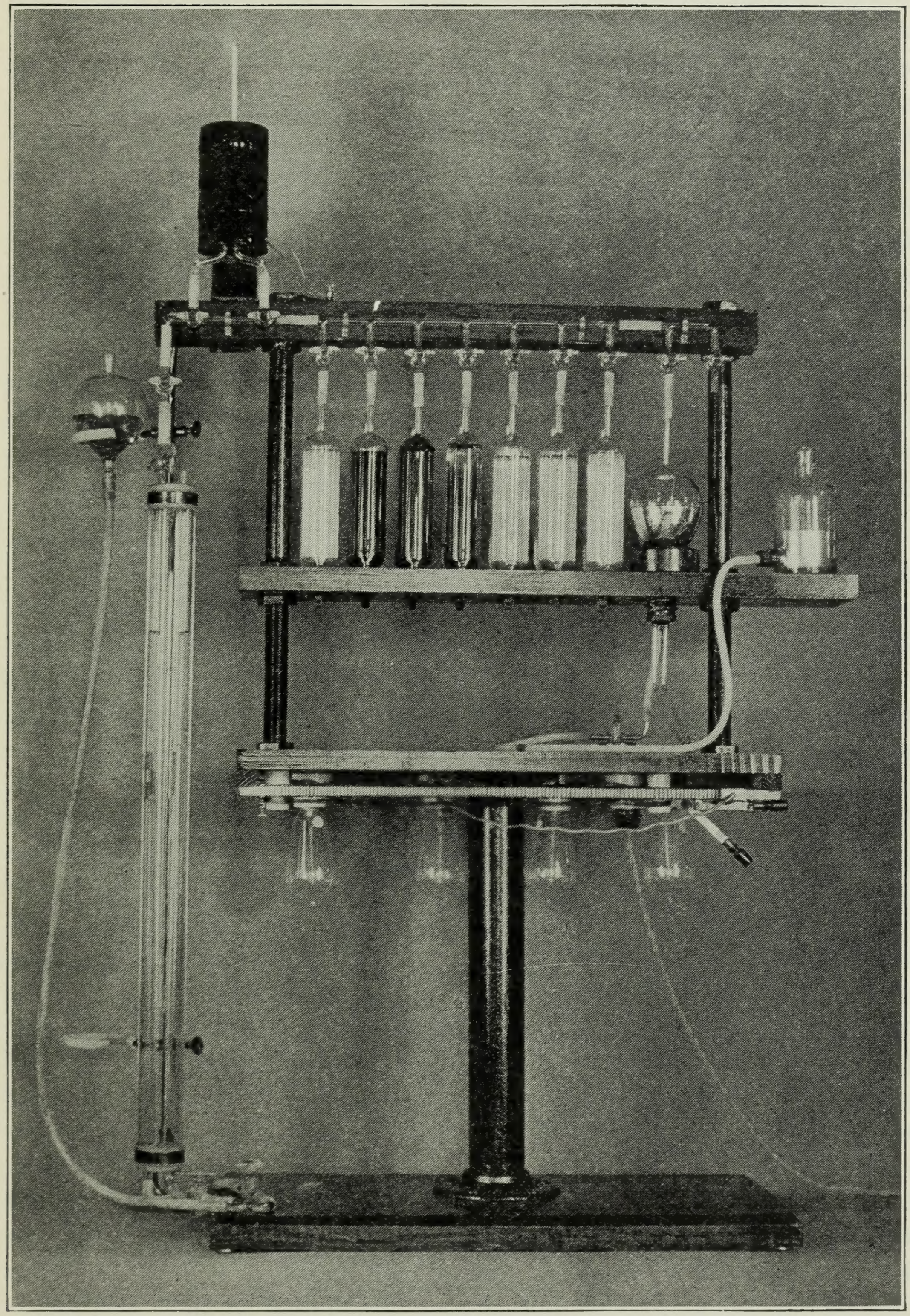

FIG. 1. MODIFIED ORSAT APPARATUS

the absorption processes, designated by the several constituents to be determined, are arranged in their order of analysis as follows: (1) carbon dioxide, (2) oxygen, (3) ethylene, (4) benzene, (5 and 6) carbon monoxide. Pipette No. 7 is for the purpose of storing the gas to be used in the combustion processes. The pipette at the extreme right, No. 8, is the slow combustion pipette; the combustion process is by means of a platinum spiral over mercury. The copper oxide furnace, shown at the left and on top of the apparatus, is used for the selective combustion of hydrogen, at a temperature not exceeding 300 deg. C. and, in the order of analysis, follows the determinations (3) and (4) of the "heavy hydrocarbons," or "illuminants." The temperature control for either combustion unit is shown on the main support attached to the central pedestal. The water jacketed burette with leveling bulb at the left may carry either mercury or water as desired.

4. *Illinois Apparatus.*—The apparatus, Fig. 2, which has been developed from the enlarged Orsat is the same as that shown in Fig. 1 except that all of the absorption pipettes are replaced by an absorption burette of the Morehead type. The copper oxide furnace and the slow combustion pipette with the platinum spiral are retained. The Morehead burette serves as a measuring burette and as an absorbing pipette for carbon dioxide, illuminants, oxygen, and carbon monoxide. It is surrounded by a jacket, filled with water slightly acidulated to keep it clear. The leveling bulb L_1 is used to obtain atmospheric pressure on the gas for measurement, and to force the gas through the copper oxide furnace or into the slow combustion pipette. The inner funnel M is connected to the burette by a ground glass joint so that it may be easily removed. The outer funnel N is fastened to the capillary of the burette by a rubber stopper and is connected to the overflow cup O by glass tubing. This funnel catches and carries away the solution when funnel M is removed for cleaning. Overflow cup O serves as a seal to the burette and to conduct the waste solution to the sink. The siphon leading away from this receptacle draws the solution from the bottom and when this solution reaches a certain height the overflow through the siphon begins. When the solution is lowered to about one-half inch above the bottom of stopcock A the flow is broken by means of a small tube sealed into the top of the S of the siphon and extending down the proper distance in the overflow to break the siphon at the desired level.

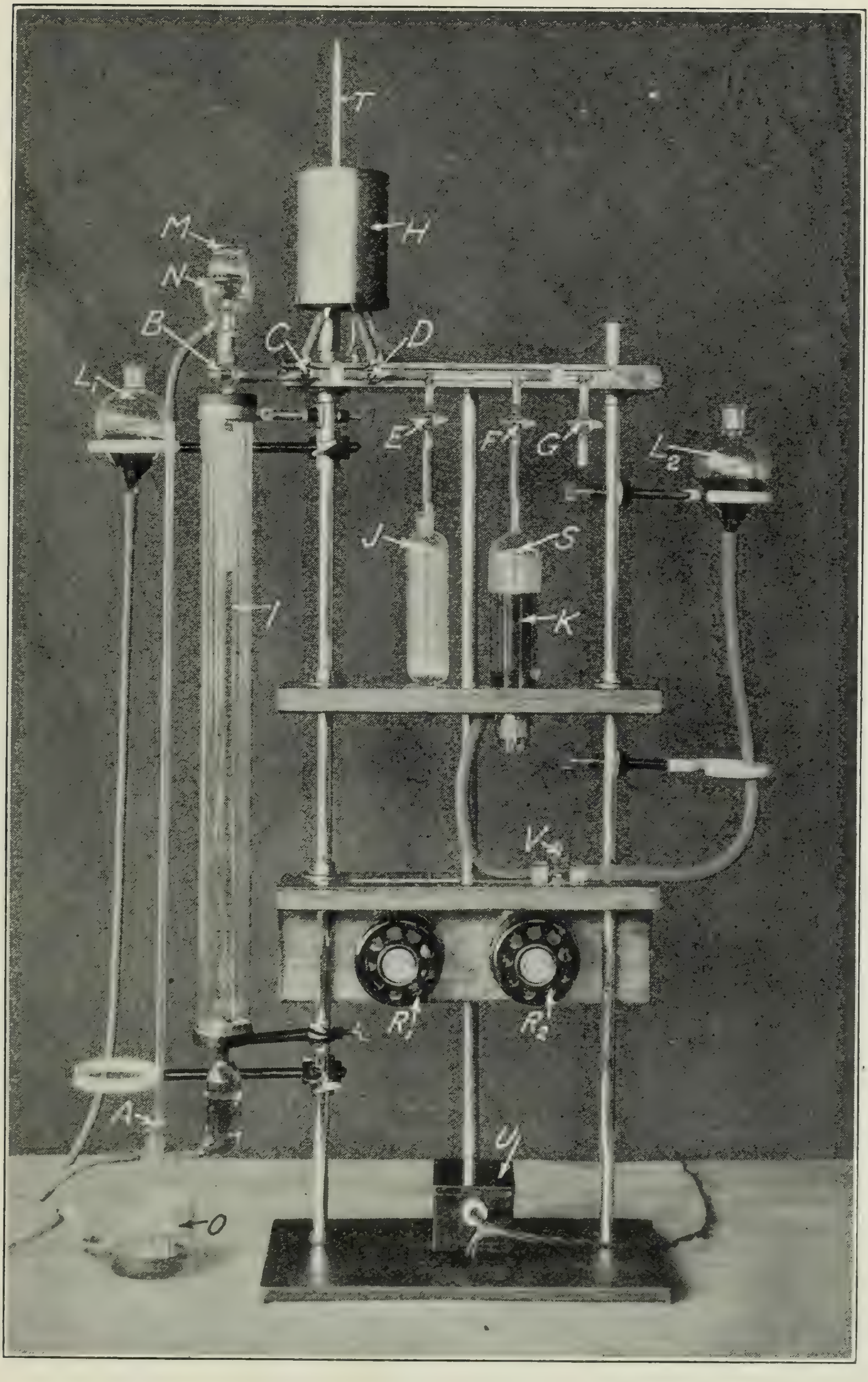

FIG. 2. ILLINOIS GAS APPARATUS

The copper oxide furnace *H* consists of a chromel wire resistance wound on an alundum core, insulated with sil-o-cel and contained in a metal jacket. In this furnace No. 26 Chromel "A" wire is used, of suitable length to furnish about 150 ohms resistance. The current is taken from a 110-volt a-c. lighting circuit. A 360 deg. C. thermometer *T* extends down through the furnace about half way and rests against the U-tube. The heating element or furnace proper is removable. The U-tube of pyrex glass is filled completely with copper oxide which has been ground to pass a 10-mesh sieve and to be caught on a 40-mesh. The oxide may either be revived from time to time by passing oxygen through it while it is at 300 deg. C., or the tube may be refilled with fresh oxide. The limbs of the tube are large enough to permit 10-mesh oxide to pass. The ends of the tube are filled with glass wool to prevent the oxide from falling out and to decrease the unoccupied space.

The slow combustion pipette *K*, holding approximately 210 cc., is made of pyrex glass. The connection to the manifold is by means of a capillary so that the gas enters the pipette in a small jet, and this aids in the prevention of explosive mixtures during the manipulation. Near the bottom of the pipette is a side arm for connection with the leveling bulb. The opening at the bottom of the pipette is thus closed with a two-hole rubber stopper which accommodates only the two glass tubes, at the inner ends of which special leading-in wires are sealed. These wires support the platinum coil *S* placed about one-half inch below and slightly to one side of the opening of the capillary tube. It is connected to a 0.65 ohm rheostat R_2 which is in turn connected to a transformer *U*, reducing the 110 to 6 volts. One plug connection serves both heating systems.

The pipette *J*, of approximately 100 cc. capacity, is used as a reservoir when passing the gas back and forth through the copper oxide and also for storing the gas when oxygen for the slow combustion is being measured into the burette. It is filled with distilled water slightly acidified.

The manifold connecting these parts and carrying the five stopcocks is made of capillary tubing and is divided into two parts to facilitate manufacture, assembling, and repairing.

For convenience in following the directions for the operation of the apparatus, the stopcocks are lettered serially *A* to *G*, beginning with the cock at the lower end of the burette as *A*. The heater is *H*, the leveling bulbs are L_1 and L_2, and the rheostats are R_1 and R_2.

IV. Manipulation of Illinois Apparatus for Fuel Gas Analysis

5. *Preparation of Reagents.*—(1) Sodium hydroxide; 10 per cent by weight of NaOH to 90 per cent distilled water.

(2) Bromine water; made by filling funnel *M* with distilled water and adding 5 or 6 drops of liquid bromine.

(3) Alkaline pyrogallate; made by dissolving 15 grams of pyrogallic acid in 100 cc. of a solution of potassium hydroxide, 1 part KOH to 2 parts water. This solution must be kept tightly stoppered.

(4) Acid cuprous chloride; made by dissolving 20 grams of powdered cuprous chloride in 100 cc. of concentrated HCl. Metallic copper should be added to keep the solution in the cuprous form.

(5) Sulphuric acid; a 10-per-cent solution of sulphuric acid should be on hand to make the confining liquid in the burette acid before combustion of the paraffins.

(6) Oxygen from a commercial cylinder is used for the slow combustion pipette. It is well to store this gas in aspirator bottles over water since it cannot easily be taken direct from the cylinder on account of the high pressure.

(7) Nitrogen is used for sweeping the manifold and copper oxide tube before starting the analysis, and after the combustion of hydrogen over the copper oxide. It may be obtained from the air by taking out the oxygen with pyrogallate, or purchased commercially in cylinders. In the latter case the residual oxygen which accompanies the nitrogen should be removed by passing through pyrogallate.

(8) The amount of mercury required for use in the slow combustion pipette is 8 pounds. It is preferable to use purified mercury.

(9) The granular copper oxide with which the U-tube in the copper oxide furnace is filled should pass through a 10-mesh sieve and be caught on a 40-mesh. After filling the U-tube with oxide, glass wool should be packed into the ends to prevent the oxide from falling out.

6. *Manipulation of Apparatus.*—In starting an analysis, the current to the copper oxide furnace is first turned on. The rheostat R_1 is connected in series with the furnace for controlling the temperature to 300 deg. C. and below. To heat the furnace quickly, all outside resistance may be cut out by turning the knob to the left, or anti-clockwise, as far as it will go. This will heat the furnace higher than 300 deg. C. To hold the temperature at 300 deg. C. or below, the knob is turned to the right, or clockwise, so that practically all of the resistance is in the circuit.

If the knob is turned clockwise the entire distance to the stop, the circuit is broken, the last few degrees on the dial serving as a switch. With the dial turned so that none of the resistance is in the circuit, the furnace will heat to about 290 deg. C. in about 20 minutes. With approximately half the outside resistance in the circuit the temperature will remain constant at 300 deg. C. Occasional attention to thermometer and rheostat will serve to control the temperature within the desired limits, viz: 250 to 312 deg. C. Because of the expansion of the gas in the tube, it is advisable to have the furnace up to temperature before starting the analysis so as to avoid a change in the volume of the gas when stopcocks *C* and *D* are opened.

While the furnace is heating, care should be taken that none of the stopcocks leak or otherwise need attention. The mercury in the capillary leading from the combustion pipette is raised to a point just below the rubber joint. The water in pipette *J* is brought to a similar level, and both points are marked permanently with a file or a blue pencil. Care must be taken not to turn on the current when the combustion pipette is filled with mercury, as so doing will cause a short circuit and damage to the apparatus. The manifold and copper oxide tube are swept out thoroughly with nitrogen, drawn in through stopcock *G* and expelled through stopcock *B*. Burette *I* is completely filled with slightly acidulated water to the end of the capillary.

To take a sample of gas, funnel *M* is removed and in its place the rubber sampling tube, which has been thoroughly flushed out with the unknown gas, is connected. Stopcock *B* is turned so that the half-bore is to the left and the through-bore vertical. Stopcock *A* is turned so as to connect the burette with the leveling bulb, and the latter lowered to create suction. Slightly more than 100 cc. of gas is drawn in and stopcock *B* closed, by turning to the right, or clockwise. The sample tube is disconnected, the solution in the leveling bulb brought slightly above the level in the burette, stopcock *B* slightly opened, and the gas slowly released until there are 99.8 cc. left in the burette at atmospheric pressure.*

The temperature of the heater is observed, and rheostat R_1 adjusted if necessary.

7. *Determination of Carbon Dioxide.*—Now that the apparatus contains exactly 100 cc. of gas, the next step is to remove the carbon dioxide.

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*The total capillary at the top of the burette ordinarily holds 0.2 cc. and this is swept into the burette when the first reagent is run into it, thus providing the full 100 cc. of gas taken. If the capillary space varies from 0.2 cc. the necessary allowance is made in the original reading of 99.8 cc.

Funnel *M* is nearly filled with a 10-per-cent NaOH solution. Stopcock *A* is turned so as to connect burette with drain trap. In each process of absorption it is essential that stopcock *A* be opened to the drain trap before stopcock *B* is opened, otherwise the gas might be under pressure and escape through the solution in funnel *M*. Stopcock *B* is turned so that the NaOH solution trickles slowly down the sides of the burette, thus giving the maximum absorption area. (Note: All of the solution should not be run into the burette, as air would enter and spoil the analysis.) When all but a few cc. have run out, stopcock *B* is closed. By lifting funnel *M* from its support, the remaining NaOH solution is emptied into funnel *N*; funnel *M* is then replaced and filled with distilled water. All traces of the NaOH solution are washed out by allowing the water to run slowly down the sides of the burette. After stopcock *B* is closed the water is permitted to drain from the sides of the burette, then stopcock *A* is turned to connect with the leveling bulb, and atmospheric pressure obtained by equalizing the levels.* The reading is taken. The difference between this and 100 represents the percentage of carbon dioxide.

The temperature of the heater is observed.

8. *Determination of Illuminants.*—The illuminants are next removed by bromine water. Funnel *M* is three-fourths filled with distilled water and 5 or 6 drops of liquid bromine added. Stopcock *B* is opened very slightly so that the bromine falls *very slowly,* thus giving it time to vaporize before reaching the liquid in the burette. It will be noted that the bromine fumes cause expansion of the gas volume. After a minute or so is allowed for the reaction, water is admitted to the burette, which absorbs the bromine fumes and thus gradually decreases the volume of the gas. It is well to admit a second funnel of distilled water, followed by one-half funnel of sodium hydroxide. This assures the complete removal of bromine fumes and avoids a gummy deposit on the sides of the burette. The gas is brought to atmospheric pressure and the reading taken. The difference between this and the previous reading represents the percentage of illuminants (ethylene and benzene).

The temperature of the heater is observed.

9. *Determination of Oxygen.*—Oxygen is next removed by admitting slowly about three-fourths of a funnel of alkaline pyrogallate and allowing it to trickle down the sides of the burette. The tendency of pyrogallate is to run down in a small stream. This can ordinarily be avoided by working stopcock *B* slightly, thus running the solution in faster or slower. Funnel *M* and the sides of the burette are carefully washed

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*Before each reading of the gas volume in the burette sufficient time should be allowed for the liquid on the sides of the burette to drain.

with distilled water followed by a cup of 10-per-cent sulphuric acid to clear up the solution in the burette. The gas is brought to atmospheric pressure and the reading taken. The difference between this and the previous reading represents the percentage of oxygen.

10. *Determination of Carbon Monoxide.*—Carbon monoxide is removed by an acid solution of cuprous chloride. Three-fourths of a funnel is usually sufficient as the absorption is rapid and complete. This solution forms a light white precipitate with the confining liquid in the burette and this should be washed out before proceeding further. Three or four funnels of distilled water are usually enough to clear the solution. It is also well to flush out the waste cup several times with water at this point in order to clear it. If it is thought that this amount of water has not removed all the hydrochloric acid fumes remaining from the acid cuprous chloride, a small amount of sodium hydroxide may be run through funnel *M*. This may produce a precipitate in the burette, which can be cleared by running in dilute sulphuric acid. The pressure is equalized and the reading taken as before. The difference between this and the previous reading represents the percentage of carbon monoxide.

This concludes the absorption procedure.

11. *Determination of Hydrogen.*—The next step is the determination of hydrogen by means of the copper oxide furnace *H*. The furnace should be at 300 deg. C. or slightly below. To make sure that there is no pressure in the copper oxide tube, stopcock *D* is turned from the off position shown in the figure (the half-bore in the stopcock is pointing down) to connect the copper oxide tube outward through the manifold to the right. Then stopcock *G* is opened and closed immediately. Funnel *M* is nearly filled with distilled water (as a seal) and with stopcock *A* open to the drain trap, stopcock *B* is turned to connect the burette with the manifold. Stopcock *C* is turned to open from the burette to the copper oxide tube, then stopcock *A* is turned to connect with the leveling bulb. With the bulb raised to give pressure, stopcock *E* is opened. The gas passes from the burette through the copper oxide tube into the reservoir *J*. By means of the leveling bulb the gas is run back and forth through the copper oxide from six to ten times or until a constant reading is obtained. The contraction in volume is due to the burning of hydrogen to water. (Note: Care should be taken not to allow any of the solution in the burette or pipette to be drawn into the copper oxide.) When the volume has become constant, all the gas is

drawn into the burette and stopcock *E* is closed. The reading is taken. The difference between this and the previous reading is the percentage of hydrogen. To remove the hydrocarbons which are left in the copper oxide tube, it is swept out by drawing from 15 to 20 cc. of nitrogen through stopcock *G* into the burette. The gas is brought to atmospheric pressure by means of the leveling bulb, stopcocks *C* and *D* are closed by turning each till the half-bore is down, and the new volume of gas enclosed in the burette is read. All the gas is forced from the burette into the reservoir *J* without passing through the copper oxide tube, and stopcock *E* is closed.

12. *Determination of Methane and Ethane.*—The gas now contains presumably nothing but methane, ethane, and nitrogen. The paraffins are determined by burning in an atmosphere of oxygen in the slow combustion pipette *K*, ignited by the electrically heated platinum coil *S*. With the gas containing the paraffins stored in pipette *J*, about 90 cc. of oxygen is measured into the burette. Then by lowering the mercury leveling bulb to the bottom support and opening stopcocks *F* and *V*, all of the oxygen is drawn into the pipette *K* above the mercury. Stopcock *F* is closed. About 18 cc. of the gas stored in reservoir *J* is drawn back into the burette. If the gas is thought to contain a high percentage of paraffins, the platinum coil is heated to a full red by turning the knob of the rheostat R_2 to the left, or anti-clockwise, the required distance. If the coil is heated too much by the current, the added heat produced by burning the paraffins will melt it. If the gas is low in paraffins the wire may be heated to almost a white heat without danger of burning out. Before ignition the confining liquid in the burette should be acid, to minimize the absorption of the carbon dioxide formed by combustion. To carry out the combustion, the gas is placed under pressure in the burette by opening stopcock *A* to the leveling bulb L_1 which remains on the upper support as shown in the figure. The oxygen in the mercury pipette *K* is under a vacuum due to retaining the leveling bulb L_2 at the lower position. Stopcock *B* is open to the manifold. The flow of gas into the pipette is regulated by stopcock *F* which is turned slightly so that the gas flowing past the red hot coil produces a small flame. (Note: Be careful not to allow the solution from the burette to flow into the pipette.) Before turning off the current the mercury leveling bulb is raised to the upper support so that the gas in the pipette is under pressure. The current is turned off. The hydrocarbons have burned to carbon dioxide and water, and the condensed water may be seen on the

surface of the mercury. No special attention is given to the elimination of water from pipette *K*, but it is the usual practice to bring the level of the mercury up to a mark slightly below the rubber connection after each determination, thus maintaining the water in pipette *K* at a minimum.*

13. *Calculations.*—To calculate the percentage of methane and ethane in the gas, it is necessary to know the amount of contraction and the amount of carbon dioxide formed in the combustion. Hence stopcock *F* is opened, leveling bulb L_1 lowered, and the gas drawn back into the burette. If the proper volumes of oxygen and gas were taken as directed, the burette will be able to hold all of the gas after the combustion. Stopcock *F* is closed. The gas is brought to atmospheric pressure and the reading taken. The carbon dioxide is absorbed in the same manner as described previously, and the reading taken. If a check is desired, a similar determination may be made on a part of the gas remaining in pipette *J*. From the readings taken, four values are available: (1) Volume of gas for combustion, (2) Volume of oxygen taken, (3) Volume of gas after combustion, and (4) Volume of carbon dioxide in the gas after combustion. The contraction due to the condensation of water is obtained by subtracting (3) from (1) plus (2). By substituting these values in a formula derived from the chemical equations of the reaction we have:

$$\frac{2 \times \text{contraction} - CO_2}{3} = \text{Vol. of } C_nH_{2n+2} \text{ (the paraffins)}$$

The value for n, or the index of the relative amounts of ethane and methane, will be found to be: $n = \frac{CO_2}{\text{Vol.}}$. If $n = 1$ the entire volume is methane (CH_4); if $n = 2$ the entire volume is considered ethane (C_2H_6); if $n = 1.3$, then 0.3 of the volume of the hydrocarbons is ethane and 0.7 methane; if $n = 1.6$, then 0.6 of the volume is ethane and 0.4 methane, etc. Since only a fraction of the gas left after the removal of hydrogen was taken for combustion, the volume of methane and ethane found must be multiplied by $\frac{a}{b}$ where a is the total volume of the gas stored in the pipette *J* after the removal of the hydrogen, and b is the volume of that part of the gas taken for combustion. This gives the percentage of methane and ethane in the 100 cc. of gas taken for analysis. By adding all the percentages of carbon dioxide, illuminants, carbon monoxide, hydrogen, methane, and ethane, and then subtracting from 100, the percentage of nitrogen is found.

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*In determining the paraffins the analyst should exercise caution and be thoroughly familiar with the procedure. An explosive mixture in the combustion pipette could be disastrous and might be caused by admitting the gas before heating the coil or by failure to heat the coil sufficiently to ignite the gas when it first enters the pipette.

After the analysis the current to the copper oxide furnace is turned off, the mercury lowered from the platinum coil, the burette and leveling bulb L_1 flushed out with water, and stopcocks *G* and *D* opened to the copper oxide furnace so that the contraction on cooling will not cause breaking.

14. *Typical Analysis.*—Table 1, illustrating a typical coal gas analysis, shows the methods of recording readings and calculations.

TABLE 1
A TYPICAL COAL GAS ANALYSIS
Illustrating Calculations for Paraffins

Constituents	Volume 100 cc.	Per cent	Calculations
Carbon dioxide	98.4	1.6	
Illuminants	93.6	4.8	
Oxygen	92.4	1.2	
Carbon monoxide	84.0	8.4	
Hydrogen	37.7	46.3	
			$V = \frac{2C - CO_2}{3}, n = \frac{CO_2}{V}$
New volume adding Nitrogen	50.5		
Oxygen added	99.8		$\% = \frac{a}{b} \times V$
Gas taken	18.2		$V = \frac{40.4 - 10.2}{3} = 10.0$
Total	118.0		
After combustion	97.8		$n = \frac{10.2}{10} = 1.02$
Contraction	20.2		
After Sodium Hydroxide	87.6		$\% = \frac{50.5}{18.2} \times 10 = 27.7$
Carbon dioxide formed	10.2		
Methane		27.2	$27.7 \times 0.02 = 0.5$
Ethane		0.5	
Nitrogen		10.0	
Total		100.0	

V. SUMMARY

15. *Summary.*—The Illinois apparatus, when operated as described, has certain features of advantage which may be summarized as follows:

By use of the Morehead type of burette the multiplication of absorption pipettes is avoided. This permits the use of a shorter manifold with a minimum number of stopcocks and rubber connections which are always to be avoided in a gas analysis apparatus.

The ordinary Morehead burette is equipped with platinum contacts for use as an explosion burette. The uncertainty of complete combustion and other operating difficulties make it desirable to carry out the combustion processes in other ways; hence the slow combustion pipette has been adopted for handling the paraffin hydrocarbons. By reason of the selective action of copper oxide at definite temperatures the introduction of the copper oxide furnace for hydrogen combustion will be found a great improvement.

With water as the leveling liquid in the burette it is better to make the carbon monoxide determination by the absorption method than by the combustion method, owing to the solubility in water of the carbon dioxide formed.

The use of fresh absorbing solutions for each determination obviates the uncertainty of old and partially saturated reagents. This practice does not require in the aggregate a larger consumption of chemicals than is the case with the ordinary absorption pipettes.

The time element in carrying through an analysis is in favor of the apparatus as described.

APPENDIX A

Methods of Fuel Gas Analysis

A résumé is here made of the methods employed in gas analysis. The purpose of the review has been to list in readily available form those processes which seem to have a good basis for their status in the literature of gas analytical processes, with an indication, where numerous methods are in vogue, as to a preference in the matter of procedure. In a number of instances an experimental study has been made in the way of testing certain features which might be open to question.

It may also be noted that in indicating a choice of methods the practicability of the method, with the type of apparatus ordinarily available, has been the ruling factor which has governed the choice in each instance.

According to the manner of determining the constituents of a gas, a classification of methods may be made as follows:

(1) Fractionation by low temperature methods
(2) Optical methods, using the interferometer
(3) Absorption methods
    (a) By titration
    (b) By difference in volume
(4) Combustion methods
    (a) By explosion, using the electric spark
    (b) By slow combustion over a red hot platinum coil
    (c) By combustion over cupric oxide

1. *Fractionation by Low Temperature Methods.**—The analysis of fuel gas may be made by freezing out the condensable gases by means of liquid air or solid carbon dioxide. The condensable gases are carbon dioxide, water vapor, ethane, ethylene, acetylene, and benzene; those which are noncondensable, within the range of practicability, are hydrogen, methane, carbon monoxide, nitrogen, and oxygen. The liquid obtained is submitted to a process of separation by fractionation. This method, using 1000 liters of gas, it is claimed, admits of the most complete analysis of fuel gas possible, but because of the time required and the involved manipulation it is not applicable to technical gas analysis.

2. *Optical Methods.*†—The interferometer making use of the difference in the refractive indices of gases is applicable to a limited extent

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*Labean and Damiens, Compt. Rend. clvi, p. 797, and clvii, p. 144. Czako—J. f. Gasbeleucht, 1913, p. 1192.

†Technical paper 185, Bureau of Mines. Technical paper 131, Bureau of Standards.

in gas analysis. The refractive indices of the gases should differ in the fourth decimal place to admit of a good analysis, but several of the constituents in fuel gas differ very little even in the fifth decimal place, so that the interferometer cannot be used satisfactorily in the complete analysis of fuel gas. It can be used in the determination of carbon dioxide in mine gases; in determining the purity of hydrogen, that is, its freedom from oxygen and nitrogen; in determining the degree of carburization of illuminating gas by gas oil; and in determining the amount of ammonia in gases.

3. *Absorption Methods.*—

By Titration

A known volume of gas is passed through a standard solution (normal or 0.1 N) which absorbs all of the gas to be determined, and the excess solution is determined by titration. For example, carbon dioxide is absorbed in normal baryta water, and normal oxalic acid with phenolpthalein as the indicator is used for titration. Another example is the determination of benzene* in the presence of other unsaturated hydrocarbons. The total amount of heavy hydrocarbons is absorbed in fuming sulphuric acid and the ethylene in another sample is determined by absorption in bromine water of known strength, and titration of the residual free bromine is made with sodium thiosulphate. If only benzene and ethylene are present the amount of benzene is equal to the difference between these two results. These two gases are the only ones in fuel gas which are mentioned in the literature as being determined by titration. This method for carbon dioxide is not as quick as direct absorption and measuring the difference in volume. The titration for benzene is accurate but it is indirect and takes considerable time. In technical gas analysis titration methods are not used.

By Difference in Volume

In this method the mixture of gases is treated with a series of absorbents. The difference in the volume of the gas before and after it has been acted upon by each absorbent represents the amount of some particular constituent in the fuel gas. The absorption may take place in the burette itself as in the case of the Morehead burette, or in separate absorption vessels as in the case of the modified Orsat apparatus or the Hempel pipettes.

In this discussion a fuel gas will be taken which is assumed to have the following constituents: carbon dioxide, ethylene, benzene, oxygen, carbon monoxide, hydrogen, methane, ethane, and nitrogen. Carburetted water gas or coal gas will contain all of these constituents. Acetylene is very seldom present in fuel gas and the higher homologues of the paraffin hydrocarbons are present in such small quantities, except possibly in natural gas, that they are not here considered. Out of this list of gases carbon dioxide, ethylene, benzene, oxygen, carbon monoxide, and hydrogen can be absorbed. The possibility of absorbing methane, ethane, and nitrogen will be discussed later.

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*J. f. Gasbeleuchtung, 39, p. 799, 1896; 43, p. 347, 1900.

Order of Absorption of Gases

A solution for absorbing one gas must not absorb any of the other gases remaining in the mixture. For example, potassium hydroxide must not absorb oxygen or carbon monoxide, but it is permissible for cuprous chloride to absorb oxygen and illuminants as well as carbon monoxide, because in the order of analysis oxygen and illuminants have already been removed. If a water solution is used in the burette and reservoir as the confining liquid, the gases most soluble in water must be taken out first. It will be helpful in this connection to have at hand a table of gas solubilities. The following table gives the amount of gas soluble in 1 cc. of water at 15 deg. C.

TABLE 2

COMPARISON OF SOLUBILITIES OF GAS CONSTITUENTS

Fuel gas	Amount soluble in 1 cc. water at 15° C. cc.
CO_2	1.003
C_2H_4	0.161
C_6H_6 vapor	Fairly soluble*
C_2H_6	0.0541
CH_4	0.0369
O_2	0.0341
CO	0.0254
H_2	0.0188
N_2	0.0168

*Treadwell-Hall, Vol. II, pp. 753-4.

Carbon dioxide being very soluble in water must be removed first, then the illuminants, ethylene and benzene, next. In common practice oxygen, carbon monoxide, and hydrogen are removed fourth, fifth, and sixth, then methane and ethane together as seventh and eighth. The order of removal is thus:

$$
\begin{array}{lll}
(1)\ CO_2 & (4)\ O_2 & \begin{matrix}(7)\\(8)\end{matrix}\left\{\begin{matrix}CH_4\\C_2H_6\end{matrix}\right. \\
\begin{matrix}(2)\\(3)\end{matrix}\left\{\begin{matrix}C_2H_4\\C_6H_6\end{matrix}\right. & \begin{matrix}(5)\ CO\\(6)\ H_2\end{matrix} & (9)\ N_2
\end{array}
$$

Oxygen has practically the same solubility as methane, so it would not matter which gas was removed first. Carbon monoxide and hydrogen are almost insoluble in water so the percentage of these gases would be unaffected by the use of water as the confining liquid. Since methane and ethane are preferably removed by a combustion process the removal of oxygen, carbon monoxide, and hydrogen must precede their determination, though the strict order of solubilities would reverse that procedure. However, the range of difference is not great enough to entail appreciable error. Evidently, if extreme accuracy is desired in a gas analysis mercury should be used as the confining liquid. However, with water as the confining liquid and processes used involving a minimum of time, results of a high degree of accuracy are possible. In the Morehead type of burette the leveling bulb is not moved during the absorption of one gas and is only used as a device for obtaining atmospheric pressure. Furthermore, very little liquid is in contact with the gas.

Carbon Dioxide, CO_2

Density 1.529 (air = 1) Molar volume 22.26 l. Carbon dioxide is absorbed in a strong solution of either caustic soda or caustic potash. For use in pipettes this solution is made by dissolving 1 part of the hydroxide in 2 parts of water. A solution of this concentration of potassium hydroxide has an absorbing power of 40. Since caustic soda is cheaper than caustic potash, a 10-per-cent solution of sodium hydroxide is used in the Morehead burette where the absorbent is lost. It has a greater chemical action on glass and forms a bicarbonate more quickly than potassium hydroxide, but this is not a disadvantage in the Morehead type of absorption. The absorption by potassium hydroxide is very rapid. Lunge* gives one minute as ample time and White† indicates three minutes as sufficient in all cases. It is advisable if the concentration of carbon dioxide is fairly high to pass the gas into the potassium hydroxide pipette (containing glass tubes for a better absorption surface) five or six times. Concentrated caustic solutions dry the gas so that it is best to let it stand in the burette before reading the volume until it has again become saturated with moisture. These solutions also absorb other acid gases such as hydrogen sulphide, sulphur dioxide, chlorine, etc.

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*Lunge, "Technical Gas Analysis," p. 117.
†White, "Gas and Fuel Analysis," p. 28.

Unsaturated Hydrocarbons

The unsaturated hydrocarbons, ethylene C_2H_4, benzene C_6H_6, and acetylene C_2H_2, are often designated as heavy hydrocarbons or illuminants.

Ethylene, C_2H_4

Density 0.9739 (air = 1) Molar volume 22.27 l. Fuming sulphuric acid (with 20 to 25 per cent free sulphur trioxide) absorbs 8 times its volume of ethylene. Ethionic acid, $C_2H_6S_2O_7$, is formed. If the acid is strong 3 to 4 transfers into a pipette (containing glass tubes to increase the absorption surface) is sufficient for a complete absorption of ethylene. The sulphur trioxide fumes must be removed in the potassium hydroxide pipette before reading the volume absorbed. Bromine water rapidly and completely absorbs ethylene with the formation of ethylene bromide, $C_2H_4Br_2$. Dennis* and White† prefer the reagent made by diluting saturated bromine water with twice its volume of water, while Lunge‡ uses a saturated solution of bromine in water, with a small excess of bromine. Both solutions will give good results but the weaker the solution the longer it takes to brominate the ethylene. As long as this solution is saturated with bromine or one-third saturated it will absorb ethylene indefinitely. The bromine fumes must be removed by contact with potassium hydroxide solution.

Benzene, C_6H_6

Molar volume C_6H_6 vapor = 22.39 l. Liquid benzene is soluble in alcohol, ether, carbon bisulphide, caoutchouc, ethylene bromide, bromine, and fuming sulphuric acid. Benzene vapor is soluble in these absorbents, and also in paraffin oil and concentrated nitric acid. Alcohol, ether, and carbon bisulphide could not be used, of course, because they are volatile and would add some of their vapor to the gas. Paraffin oil requires the absorption to be carried on below 0 deg. C. Nitric acid cannot be used when carbon monoxide is present because carbon monoxide is oxidized to carbon dioxide and would thus be removed with the benzene when the acid vapors are passed into the caustic potash solution. Caoutchouc is to be avoided in gas analysis. Ethylene bromide has little advantage over bromine water. Dennis and O'Neill§ have used nickel ammonium cyanide for absorbing benzene, $Ni(CN)_2.NH_3.C_6H_6$

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*Dennis, "Gas Analysis," p. 249.
†White, "Gas and Fuel Analysis," p. 28.
‡Lunge, "Technical Gas Analysis," p. 119.
§Dennis and O'Neill, J. Am. Chem. Soc. 23, p. 503, 1903.

being formed. Dennis speaks very highly of this method for benzene, but it has met with much criticism. Experiments conducted in connection with this work seem to indicate that a constant volume could not be obtained after five two-minute intervals in the 5-per-cent sulphuric acid solution.

Fuming sulphuric acid readily absorbs benzene, forming benzene sulphonic acid $C_6H_6SO_3$. It absorbs about the same amount of benzene as it does of ethylene. The absorbing power is about 8. If the concentration of benzene in the gas is not more than 10 per cent, three to five passes into fuming sulphuric acid will absorb all of the benzene. The sulphur trioxide fumes must be removed by potassium hydroxide. Fuming sulphuric acid absorbs moisture readily, so the pipette should be stoppered when not in use.

Benzene is neither brominated nor oxidized by bromine at ordinary temperatures. Haber† suggested, and it is now accepted that the absorption of benzene by bromine is of a purely physical nature. If such is the case then the more concentrated the bromine solution the more complete would be the removal of the benzene. While bromine water even as a purely physical reagent seems to absorb benzene quantitatively,* it is not considered as good as fuming sulphuric acid with which the benzene chemically combines.

Acetylene, C_2H_2

Density 0.9134 (air = 1) Molar volume 22.03 l. Acetylene is readily absorbed by fuming sulphuric acid, acetyl sulphuric acid $C_2H_4SO_4$ being formed; it is also absorbed in bromine water but the reaction is very slow in the cold. Ammoniacal cuprous chloride absorbs acetylene as it does ethylene and benzene. Acetylene is present in such small quantities in carburetted water gas and coal gas that it is not an important constituent. Further information concerning acetylene is given in Dennis† and Treadwell-Hall.‡

Separation of Benzene from Ethylene

Benzene is usually present in carburetted water gas and coal gas in varying amounts, generally between 0.4 and 2.0 per cent. Benzene has such a high calorific value (3809 B.t.u. per cu. ft. at 60 deg. F., 30 in.)§ that an analysis should show even such small quantities as 0.5 per cent. To separate it from ethylene, however, is a difficult problem.

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*Haber. Treadwell-Hall, Vol. II, p. 753.
†Dennis, "Gas Analysis," pp. 250-3.
‡Treadwell-Hall, Vol. II, pp. 754-6.
§Parr, "Fuel, Gas, Water and Lubricants," p. 101.

Many attempts to separate benzene from ethylene have been made, but they do not seem to be suitable for commercial analysis where only 100 cc. of the fuel gas is used. Alcohol would dissolve both gases and some of the other gases present. Paraffin oil has to be cooled below 0 deg. C. and a large quantity of gas passed through it, so that its use involves too long a procedure to introduce into the usual scheme of gas analysis. Fuming nitric acid forms dinitrobenzene but it also oxidizes carbon monoxide to carbon dioxide. Ammonium nickel cyanide is not satisfactory because of the gradual decrease in volume on successive passes into it and then into the sulphuric acid. Anderson* gives a good review of the literature and proposes a scheme of estimating benzene in a gas by placing a measured quantity of gas containing an unknown amount of benzene vapor in contact with benzene in a special apparatus and noting the increase in volume. By determining what the increase in volume would have been had the gas contained no benzene vapor the amount of benzene vapor actually present can be computed. Apparatus for standardization has not been developed and the method is not in use at present. The difficulty of finding out how much benzene the gas would absorb if no benzene were present would be a serious one. The method would involve temperature and pressure determinations; and the necessity of removing other gases in the original gas before adding the benzene would complicate the procedure. Benzene is absorbed by charcoal, but other gases in the mixture would also be absorbed in small quantities.

Haber and Oechelhauser† have devised a method which is accurate and to be recommended for exact analysis, but it involves rather a long procedure for technical gas analysis. In one portion of the gas, the sum of the ethylene and benzene is determined by absorption with bromine water or fuming sulphuric acid, while in a second portion the gases are absorbed in titrated bromine water, and the excess of the latter determined by titrating the iodine liberated from potassium iodide solution (to which the bromine solution has been added) with sodium thiosulphate.

$$1 \text{ cc. } \frac{N}{10} I_2 = 1.114 \text{ cc. } C_2H_4 \text{ at } 0° \text{ C., and } 760 \text{ mm.}$$

$$C_2H_4 + 2Br_2 \rightarrow C_2H_4Br_2 + Br_2$$

$$Br_2 + 2KI \rightarrow 2KBr + I_2$$

$$I_2 + Na_2S_2O_3 = \text{percentage } I_2$$

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*R. P. Anderson, J. Ind. and Eng. Chem., 10, pp. 25-26, 1918.
†Haber and Oechelhauser, J. f. Gasbeleuchtung, p. 804, 1896.

The percentage I_2 gives the percentage of free Br_2 present and from this is derived the amount of combined Br_2. The difference between the amount of ethylene found in the titration and the sum of the two absorbed in fuming sulphuric acid gives the amount of benzene present. The objection to this method is that it is indirect for benzene and that a determination takes considerable time.

Taplay* separates ethylene from benzene by passing the gas into a solution made up of 1 volume of saturated bromine water diluted with 4 volumes of water (White used 1 to 3). This solution removes ethylene. He then passes the gas into a solution consisting of 560 cc. of water, one-half lb. of potassium bromide, and 115 gr. bromine. This removes the benzene. This method of using a concentrated solution of bromine water with potassium bromide has not been studied in this connection, but seems to be a good one.

A method for separation of the heavy hydrocarbons has been proposed whereby the ethylene is removed by a solution of bromine in water (the solution has a few drops of bromine in the bottom of the pipette). The benzene is then removed by fuming sulphuric acid.

An investigation of these methods was carried out to determine whether the saturated bromine water and fuming sulphuric acid removed the same amount of heavy hydrocarbons, and what bearing the concentration of the bromine water had on the separation. The following table shows that fuming sulphuric acid removed an average of 0.44 cc. more than saturated bromine water from 100 cc. of carburetted water gas.

TABLE 3

RELATIVE REMOVAL OF ILLUMINANTS BY FUMING SULPHURIC ACID AND SATURATED BROMINE WATER

No. of gas sample	Saturated bromine water	Fuming sulphuric acid	Per cent difference
1	12.6	12.7	0.1
2	12.2	12.3	0.1
3	11.8	12.2	0.4
4	10.8	11.0	0.2
5	10.4	11.2	0.8
6	10.2	10.5	0.3
7	9.6	10.2	0.6
8	9.1	10.0	0.9
9	9.1	9.5	0.4
10	9.6	10.0	0.4
11	9.5	10.2	0.7
			Average 0.44

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*Taplay, J., Gas Light, 118, pp. 217, 285, 1912.

The results shown in Table 4, taken from an article by Fieldner and Jones,* show an average removal of 0.6 cc. more for fuming sulphuric acid than for saturated bromine water in 100 cc. of mixed coal and water gas. These results indicate that fuming sulphuric acid removes more heavy hydrocarbons than does bromine water, presumably due to its chemical combination with both ethylene and benzene, while the action of bromine water on benzene is of a purely physical nature. M. Korbuly† explains this action by saying that just as bromine can be removed from an aqueous solution by shaking with benzene, so benzene can be removed by shaking with bromine.

TABLE 4

RELATIVE VALUE OF FUMING SULPHURIC ACID AND SATURATED BROMINE WATER FOR REMOVAL OF ILLUMINANTS, AS GIVEN BY FIELDNER AND JONES

Saturated bromine water	Fuming sulphuric acid
12.9	14.3
13.2	13.6
13.3	13.4
	13.2
Average 13.1	13.6
	14.2
	Average 13.7
Difference 0.6 cc.	

To find out the effect of concentration of bromine water on the absorption of the heavy hydrocarbons, carburetted water gas was passed into a one-third saturated solution of bromine after removal of the CO_2 and then another sample of the same gas was passed into saturated bromine water. The following results were obtained:

TABLE 5

COMPARISON OF THE REMOVAL OF ILLUMINANTS BY WEAK BROMINE WATER AND CONCENTRATED BROMINE WATER, RESPECTIVELY

No. of gas sample	⅓ concentrated bromine water	Concentrated bromine water	Difference
1	9.2	9.3	0.1
2	8.8	8.8	0
3	8.9	8.9	0

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*Fieldner and Jones. Am. Gas. Assoc. Monthly, Vol. III, p. 366.

†M. Korbuly, Treadwell-Hall, Vol. II, p. 753.

There was no difference in the amount of gas absorbed but the weaker solution required a much longer time for absorption. The gas was passed into the pipette containing the one-third saturated solution 24 times and into the saturated solution only 10 times for complete absorption. The difference between the amount absorbed in bromine water and the amount absorbed in fuming sulphuric acid is, doubtless, benzene, but it is not necessarily all of the benzene. Benzene vapor is fairly soluble in water and potassium hydroxide, and is mechanically displaced by bromine fumes; therefore, some of the benzene will be absorbed in them. If the potassium hydroxide and water used in the burette are saturated with benzene and the bromine solution gives off no bromine vapor, then the amount of benzene left for absorption in fuming sulphuric acid is very nearly the original amount in the gas. The absorption of ethylene in weak bromine water is very slow and according to Table 5 is no more accurate than with a concentrated solution. To be certain that no benzene is mechanically displaced, the bromine solution must not give off bromine fumes. Under these conditions a fair separation of ethylene from benzene, using fuming sulphuric acid to absorb the benzene, can be made. In the Morehead burette it is not possible to make this separation because the fuming sulphuric acid would generate too much heat on coming in contact with the water; hence for this type of apparatus the concentrated bromine water must be used.

Oxygen, O_2

Density 1.1053 (air = 1) Molar volume 22.39 l. Oxygen may be determined rapidly and accurately by means of various absorbents, the best of which are:

(1) Chromous chloride
(2) Solutions of ferrous salts
(3) Metallic copper
(4) Phosphorus in solution
(5) Phosphorus in solid form
(6) Sodium hydrosulphite, $Na_2S_2O_4$
(7) A strongly alkaline solution of pyrogallol.

Chromous chloride may be used for absorbing oxygen in the presence of hydrogen sulphide and carbon dioxide. Ferrous chloride and ferrous sulphate to which ammonia has been added will absorb oxygen. Metallic copper immersed in an ammoniacal solution readily absorbs oxygen but it also absorbs carbon monoxide so that it cannot be used when carbon monoxide is present in the gas. Hot metallic copper is easily oxidized by oxygen. Phosphorus in oil has been recommended but it has not come into prominent use since its suggestion in 1910, so it need not be discussed.

Yellow phosphorus combines with oxygen producing solid oxides of phosphorus and reacts with almost no other gases which might be present. The reaction can be seen, and when once started it goes to completion. The disadvantages of phosphorus are:

(1) It must be used above 15 deg. C.
(2) The concentration of oxygen must not be too high.
(3) A poison may be present, i.e., a few hundredths of a per cent of ethylene prevents the reaction between phosphorus and oxygen. Acetylene, benzene, and hydrogen sulphide are other poisons.

A good discussion of the preparation of the phosphorus pipette is given in White's "Gas and Fuel Analysis."

Sodium hydrosulphite absorbs 10.7 times its volume of oxygen, reacts completely with oxygen even down to 4 deg. C., and there is no danger of formation of carbon monoxide in the process. Franzen* recommends it as a better and cheaper reagent than pyrogallol. It is prepared by dissolving 50 grams of sodium hydrosulphite in 250 cc. of water and mixing this with 40 cc. of a caustic solution which is made by dissolving 500 grams of sodium hydroxide in 700 cc. of water. The reaction with oxygen is $2Na_2S_2O_4 + 2H_2O + O_2 = 4NaHSO_3$. This reagent is highly recommended in the literature and seems to be a very good absorbent; but it is somewhat unusual and not always available. It is usually designated as the hydrosulphite. It would also be correct to call it hyposulphite, but it must not be confused with ordinary "hypo" used in photography, the formula for which is $Na_2S_2O_3$ and which is a thio salt. The formula for the reagent here referred to is $Na_2S_2O_4$ and it would be found listed as a hydrosulphite.

Alkaline pyrogallate is the most common reagent for absorbing oxygen, especially in the Orsat type of apparatus. Pyrogallol is a trihydric phenol $C_6H_3(OH)_3$ which in alkaline solution is a strong reducing agent, becoming itself oxidized to other products. It must be freshly prepared and strongly alkaline or there is danger of carbon monoxide being evolved as the oxygen is absorbed. It should be used at temperatures not below 15 deg. C. Anderson† has carried out a great deal of research on this reagent, and he recommends a solution of 15 grams of pyrogallol

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*Franzen. Chem. Berichte, 39, p. 2069, 1906.
†Anderson. J. Ind. and Eng. Chem., 8, p. 131, 1916.

in 100 cc. of a solution of potassium hydroxide of sp. gr. 1.33. Potassium hydroxide and not sodium hydroxide must be used in a solution of this concentration. One cc. of this solution will absorb 22 cc. of oxygen. At a temperature of 15 deg. C. or higher the absorption takes place quickly; at 0 deg. C. the oxygen in 100 cc. of air cannot be absorbed completely in half an hour.

Carbon Monoxide, CO

Density 0.96702 (air = 1) Molar volume 22.397 l. The usual reagent for absorbing carbon monoxide is cuprous chloride dissolved in hydrochloric acid or ammonia. The acid solution is made by dissolving 400 grams of cuprous chloride in 2000 cc. of concentrated hydrochloric acid and adding metallic copper to keep the solution in a cuprous state. Since the acid is only a solvent, its exact concentration is immaterial. The ammoniacal solution is made by dissolving 200 grams of cuprous chloride in a solution of ammonium chloride (250 gr. to 750 cc. water) and to every three volumes of this mixture adding one volume of concentrated ammonia. One cc. of this solution will absorb 16 cc. of carbon monoxide.

The absorption of carbon monoxide by means of cuprous chloride takes place according to the following equation:

$$Cu_2Cl_2 + 2CO = Cu_2Cl_2.2CO$$

The compound $Cu_2Cl_2.2CO$ is extremely unstable and can only be formed when there is a certain pressure exerted by the carbon monoxide in the gas, so that when the acid solution is used the absorption is not quantitative. When an ammoniacal solution is employed, the absorption of the carbon monoxide is almost quantitative but after such a solution has been used repeatedly it gives off some of its carbon monoxide. A gas low in carbon monoxide when passed into cuprous chloride which has been used for several analyses will increase in volume, due to the addition of carbon monoxide. It is therefore necessary to use two pipettes for a complete absorption of carbon monoxide, one to absorb most of the carbon monoxide and the other to take out the last traces. In the Morehead pipette carbon monoxide is completely removed by cuprous chloride because the confining liquid never becomes saturated with Cu_2Cl_2. 2CO to the extent that carbon monoxide is given up again to the gas. In the modified Orsat one pipette of cuprous chloride should never be used for a complete absorption of more than 35 cc. of carbon monoxide, that is, in the case of most fuel gases for more than one analysis. This first pipette could be used for absorbing the main part of the carbon monoxide in several other determinations but a second pipette of fresh cuprous chloride must be used for removing the last one or two per cent.

Cuprous chloride also absorbs oxygen, acetylene, ethylene, and benzene; they must be removed before the cuprous chloride pipette is reached. Concentrated nitric acid after long shaking completely oxidizes carbon monoxide to carbon dioxide, but the reaction is too long for use in commercial analysis and also involves further absorption of the carbon dioxide. An ammoniacal solution of cuprous chloride is best for use in closed pipettes because of its higher absorbing power and its quantitative reaction. The ammonia gas must be removed by an acid pipette before the reading is taken.

Hydrogen, H_2

Density 0.0696 (air = 1) Molar volume 22.405 l. Hydrogen is generally determined by combustion or explosion methods because of the ease of oxidation and computation of results.

Hydrogen may be absorbed by palladous oxide, palladous chloride, or a solution of colloidal palladium. White* gives complete details of this absorption. However, these reagents are so expensive and so easily poisoned by carbon monoxide, hydrogen chloride, and phosphorus fumes that they have not found much favor in technical gas analysis.

Methane, CH_4

Density 0.55297 (air = 1) Molar volume 22.363 l. No satisfactory absorbent for methane is known, so it is always determined by combustion. One hundred cc. of alcohol dissolves 52.2 cc. of methane. Alcohol would not be a satisfactory absorbent because it also dissolves ethane; the alcohol vapor would have to be removed; and the solubility of methane in alcohol is too slight to warrant its use.

Ethane, C_2H_6

Density 1.036 (air = 1) Molar volume 22.154 l. Ethane, like methane, is usually determined by combustion because no satisfactory absorbent is known. One hundred cc. of alcohol dissolves 46 cc. of ethane. The objections to the use of alcohol for absorbing methane apply also in the case of ethane.

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*White, "Gas and Fuel Analysis," pp. 38-40.

Nitrogen, N_2

Density 0.96737 (air = 1) Molar volume 22.403 l. Nitrogen is practically insoluble in aqueous solutions and organic solvents. Nitrogen may be absorbed by (1) a mixture of powdered magnesium, ignited lime, and metallic sodium heated to a bright redness; (2) metallic calcium heated to redness; (3) calcium carbide heated to 800 deg. C.; or (4) metallic titanium. At 800 deg. C. titanium begins to burn in nitrogen forming the nitride.* When heated in air a mixture of nitride and oxide results. It seems very probable that a quartz tube containing titanium heated to from 600 deg. to 800 deg. C. would remove the nitrogen. At present nitrogen is determined by difference and not by combination. There would be no particular object in obtaining the percentage of nitrogen in fuel gas by combination because certainly all gases would combine with the substance used as well as the nitrogen, except helium, neon, argon, xenon, and krypton. However, these latter gases are present in quantities too small to be considered in a technical gas analysis where the percentage of combustible constituents is desired. It would be a matter of scientific interest to know how large a volume of the zero group gases is present in manufactured fuel gas.

4. *Combustion Methods.*—

Gases Not Usually Determined by Combustion Methods

Ethylene and benzene can be determined by combustion with oxygen or copper oxide; however, such a determination would not be possible in an analysis of fuel gas, since they could not be determined by this method with both methane and ethane present at the same time. Further, because they can be satisfactorily absorbed in fuming sulphuric acid or bromine water, they are not determined by combustion with oxygen either by explosion or by slow combustion over red hot platinum or heated copper.

Since oxygen is very satisfactorily absorbed and separated from the other gases by alkaline pyrogallate, a combustion method is not necessary. Carbon monoxide may be quantitatively determined by combustion in the copper oxide furnace at the same temperature as that used for hydrogen, 300 deg. C., but, owing to the high solubility of the carbon dioxide formed, the absorption method by use of cuprous chloride is more accurate. A comparison of the absorption method with the fractional combustion of carbon monoxide and hydrogen will be given later.

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*Hopkins, "Chemistry of the Rarer Elements," p. 135.

Rules Governing Combustion Methods

(a) More than three gaseous hydrocarbons cannot be differentiated by one complete combustion.

(b) Two gaseous hydrocarbons of known composition and of the same group can always be determined by one complete combustion.

(c) Three gaseous hydrocarbons of known composition, two of which belong to the same group, can always be determined by one complete combustion.

(d) In a mixture of hydrocarbons of two groups, the percentage of each group can be determined by one complete combustion.

(e) Nitrogen does not affect the determination in any of these mixtures.

(f) Hydrogen and two hydrocarbons cannot be determined by one complete combustion.

(g) Hydrogen and one hydrocarbon may be determined by one complete combustion.

(h) Carbon monoxide, hydrogen, and methane may be determined by one complete combustion.

Carbon Monoxide, CO

In exact gas analysis where the percentage of carbon monoxide is low, iodine pentoxide at 150 deg. C. may be used. Iodine pentoxide, however, is not satisfactory for oxidizing carbon monoxide in fuel gas because the percentage of carbon monoxide is too great. Carbon monoxide may be oxidized by explosion or slow combustion over platinum and palladium in the presence of oxygen. If carbon monoxide is oxidized by explosion or slow combustion, hydrogen, methane, and ethane also are oxidized and the calculation of each constituent would be impossible. If ethane were not present the calculation could be made. Carbon monoxide is completely oxidized to carbon dioxide by copper oxide at 300 deg. C.

Fractional Combustion of Carbon Monoxide and Hydrogen*

An excellent method for the combustion of carbon monoxide is its fractional combustion with hydrogen over copper oxide at 300 deg. C. Taylor† was the first one on record to make use of the copper oxide furnace electrically heated. Burrell and Oberfell‡ were the first to combine it with the Orsat type of apparatus. Other metallic oxides may be used but they are not as reactive as copper oxide and mercuric oxide changes in volume on reduction to the metal. In order of their decreasing power of oxidation they are, cobalt oxide, mercuric oxide, nickel oxide, cadmium oxide, and lead oxide. Although hydrogen requires about 50 deg. C. higher temperature of the oxide than carbon monoxide, they are not conveniently separated in the copper oxide furnace. For that reason hydrogen and carbon monoxide are oxidized together, the hydrogen being obtained by contraction, and the carbon dioxide formed is absorbed in potassium hydroxide, thus giving the percentage of carbon monoxide present. Black copper oxide is reduced to a red oxide (cuprous oxide) and metallic copper when carbon monoxide and hydrogen are passed over it, but there is practically no change in volume; hence the results will not be affected. The paraffin hydrocarbons, methane and ethane, are not oxidized by copper oxide at 300 deg. C. Methane does not begin to oxidize below 315 deg. C.* (Campbell says there is no oxidation at 453 deg. C.), and ethane is only partially oxidized at 356 deg. C.† although the oxidation starts between 305 deg. and 356 deg. C. Thus if the temperature is kept at 300 deg. C. or lower, the paraffins are not oxidized. Fifty cc. of pure carbon monoxide is completely oxidized by copper oxide at 158 deg. C. in eight minutes. In two minutes at 250 deg. C. and also at 300 deg. C., 50 cc. of carbon monoxide is completely oxidized. Pure hydrogen is practically unoxidized at 154 deg. C., but at 258 deg. C. 50 cc. is oxidized in three minutes, and at 303 deg. C. it is oxidized completely in two minutes. All mixtures of pure carbon monoxide and hydrogen (total volume = 50 cc.) are oxidized by copper oxide at 300 deg. C. in two minutes. In fuel gas where the gas is diluted with methane, ethane, and nitrogen, a longer time is required because the unreactive gases tend to keep the carbon monoxide and hydrogen out of contact with the copper oxide. If the methane, ethane, and nitrogen make up less than 20 per cent of the original gas, three minutes is generally long enough for complete oxidation of the carbon monoxide and hydrogen. If the concentration of the inert gases is higher a longer period of time is necessary, but it should never require over 10 to 15 minutes. Fifty cc. of carbon monoxide or hydrogen is completely oxidized at 250 deg. C., but the time for complete reaction is longer than at 300 deg. C. Since methane and ethane are not oxidized at 300 deg. C., it is preferable to use the furnace at this temperature because the oxidation takes place more rapidly. After the oxidation the tube must be swept out with nitrogen so that part of the methane and ethane is not left in the furnace.

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*Vandaveer, F. E., with M. J. Bradley. Thesis for M. S., Univ. of Ill. 1923.

†Taylor, J. Ind. and Eng. Chem. 6, p. 845, 1914.

‡Burrell and Oberfell. J. Ind. and Eng. Chem., 8, p. 228, 1916.

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*Terres and Manguin. J. f. Gasbeleuchtung, 58, p. 9, 1915.

†Vandaveer, F. E. with M. J. Bradley. Thesis for M. S.. Univ. of Ill. 1923.

There are some mechanical difficulties which must be guarded against in using the copper oxide furnace. The U-tube should be filled with granular copper oxide which passes a 10-mesh screen and is caught on a 40-mesh in order to permit free passage of the gas through the oxide. Other sizes can be used, but it is not advisable to use copper oxide that passes a 40-mesh screen. The tube should be inverted to allow the water formed from hydrogen to run out. Water formed from the hydrogen or water carelessly run into the oxide from the burette will cause the oxide to cake so that no gas will pass through it. In order to control the temperature between 250 and 300 deg. C. an electric furnace should be used as the heating medium. The temperature of the oxide during a combustion *must not* exceed 310 deg. C. Reduced copper oxide may be readily re-oxidized by passing air or pure oxygen through it at from 300 to 400 deg. C. It is advisable to construct the U-tube so that it can be refilled with fresh copper oxide whenever desired, that is, the U-tube should not be permanently sealed to a capillary tube. In this type of tube the oxide can be removed when it has become caked or powdered or almost completely reduced and the tube filled with fresh oxide. When the oxide in a tube sealed to a capillary tube has become caked together or some other difficulty arises, the tube must be thrown away. A larger connecting tube adds very little to the air space in the U-tube because it can be filled with oxide and glass wool.

In this investigation* experiments have been carried out upon the action of ceric oxide, palladinized asbestos, platinum black, uranium oxide, cobalt oxide, and oxides from ignited gas mantles on copper oxide. Copper oxide plus these catalysts (except gas mantle oxides) completely oxidized carbon monoxide and hydrogen in three minutes at 250 deg. C. and in two minutes at 300 deg. C. It seems unnecessary, however, to add them to the copper oxide, since copper oxide alone will completely oxidize carbon monoxide and hydrogen in this time. Most of them are expensive. They are used in a powdered form so that they tend to slow down the passage of the gas through the mixture of oxides. The catalyst must act on the oxide to aid in its giving off oxygen, and it is difficult to see just what beneficial action these substances would have on the oxide unless they were radioactive. An inert substance would merely coat the oxide and prevent the gas to be oxidized from coming in contact with it.

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*Vandaveer, F. E., with M. J. Bradley. Thesis for M. S., Univ. of Ill. 1923

The work done recently by Pease and Taylor and by Langmuir throws light on the reduction of copper oxide by hydrogen and the chemical reaction on surfaces. The work of Pease and Taylor* shows that the reaction of copper oxide and hydrogen is auto-catalytic, copper being the auto catalyst. The reaction thus appears to take place at the copper—copper-oxide interface. This is shown by the fact that the addition of metallic copper accelerates the reaction. Water vapor interferes with the formation of the original copper nuclei from the reaction zone. When hydrogen is passed over heated copper oxide there is a short period when there is very little reaction; then, after this initial period the reaction proceeds rapidly. This induction period is attributed to (a) the initial drying of the oxide, or (b) the slow initial formation of copper which acts as a catalyst. Langmuir† explains catalytic activation as the result of differences in geometrical arrangement of the surfaces of atoms. This may be accomplished by changes during the reaction itself on the surface, or by rapid fluctuations in temperature between adjacent atoms. A surface activated for one reaction may not be for another. He goes on to explain the reaction at the boundaries of phases with particular reference to the period of induction in the reduction of heated copper oxide by hydrogen. Here the copper and oxygen are ionic by virtue of the transfer of two electrons. The oxygen ions are quite inert toward molecular hydrogen. Owing to a local imperfection a copper ion may become an atom and react as a metal by absorbing hydrogen as atoms. Atomic hydrogen may react with oxygen ions while the electrons are transferred to another copper ion. Each hydrogen molecule supplies two electrons and may convert an adjacent copper ion into an atom. Reaction therefore proceeds only at the junction between phases.

According to this explanation water should be removed as far as possible from the copper oxide during analysis and oxide slightly reduced to copper and cuprous oxide is better than fresh oxide. If a catalyst for copper oxide is necessary in the analysis for hydrogen, metallic copper seems to be the best one. This explanation of Langmuir's might hold also for the action of other oxides such as ceric oxide, thorium oxide, cobalt oxide, platinum black, palladinized asbestos on copper

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*Pease and Taylor, J. Am. Chem. Soc., 43, pp. 2179-2188, 1921.
†Langmuir. Chem. Abs. 16, p. 8, 1922.

oxide. Furthermore, a substance which would catalyze the reaction of copper oxide and hydrogen would not necessarily catalyze the reaction of copper oxide and carbon monoxide.

If carbon monoxide is to be oxidized with copper oxide the confining liquid in the burette and reservoir for exact results should be mercury. In changing carbon monoxide to carbon dioxide the solubility in water at 15 deg. C. is increased 40 times. Carbon dioxide is soluble in all aqueous solutions to a very marked degree, in organic solvents, and in non-electrolytes. It is not advisable to saturate the water with carbon dioxide because some of it is displaced by a gas free from carbon dioxide. From a study of solubility tables in literature, it appears that a concentrated solution of lithium chloride dissolves less carbon dioxide at 15.2 deg. C. than any other of the aqueous solutions. In a comparative study of methods using the same sample of gas it was not possible to obtain results for carbon monoxide by the method of absorption in acid cuprous chloride which checked with those obtained by combustion with copper oxide at 300 deg. C. It was then found that the loss in carbon monoxide was equal to the gain in hydrogen, and further investigation indicated that when the carbon monoxide was oxidized to carbon dioxide some of the carbon dioxide was absorbed in the aqueous retaining solution. When mercury was used as the leveling liquid the determination of carbon monoxide by absorption in cuprous chloride checked very closely with that by combustion with copper oxide at 300 deg. C. The best scheme of analysis in the modified Orsat apparatus is to use mercury as the confining liquid and oxidize carbon monoxide together with the hydrogen in the copper oxide tube. If aqueous solutions are used as confining liquids the carbon monoxide should be removed by a solution of cuprous chloride, and the hydrogen oxidized by copper oxide at 300 deg. C. This reaction in the modified Orsat apparatus is very slow, from 5 to 20 minutes being required for complete absorption of from 20 to 30 cc. of carbon monoxide, and the last traces have to be removed in a second pipette. In the Morehead type of burette the absorption is rapid, three to four minutes being ample time.

Hydrogen, H_2

Hydrogen may be determined by combustion with palladinized asbestos. The gas is mixed with an excess of air and passed through the tube containing the palladinized asbestos. If the asbestos is very active, combustion may begin without external heat, but to make certain, the tube is heated with a small gas flame or alcohol lamp.

This method is accurate provided the palladinized asbestos is dry and active, and the proper temperature is maintained. There is a possibility that some foreign gases may render the palladium inactive.

In the modified Orsat hydrogen is always determined by fractional combustion over copper oxide. The principles of this determination are given on page 14. In the original Morehead apparatus hydrogen and methane are determined by explosion with oxygen in the burette. It is exceedingly difficult to obtain hydrogen results by these two methods which check. The following table gives comparative results for hydrogen by these two methods in fourteen analyses.

TABLE 6

PERCENTAGE OF HYDROGEN BY EXPLOSION WITH CH_4 NEGLECTING THE C_2H_6, AS COMPARED WITH PERCENTAGE BY FRACTIONAL COMBUSTION OVER CuO AND SUBSEQUENT DETERMINATION OF CH_4 AND C_2H_6 BY SLOW COMBUSTION

Values are on Carburetted Water Gas and Coal Gas

Per cent hydrogen by explosion with pure oxygen in the Morehead burette	Per cent hydrogen by copper oxide furnace	Per cent difference
31.3	33.8	2.5
30.7	34.6	3.9
35.6	48.2	12.6*
37.0	48.7	11.7*
30.6	38.7	8.1
30.1	33.9	3.8
32.3	33.5	1.2
30.6	33.5	2.9
29.0	33.5	4.5
30.1	34.3	4.2
29.6	34.8	5.2
30.7	35.3	4.6
29.7	35.9	6.2
27.4	35.4	7.0
		Average 5.6

*Low temperature coal gas.

The hydrogen results from the Morehead burette would be somewhat low because the amount of ethane in the gas is not obtained in that method. But since there was not more than 2.5 per cent of ethane in the gases used, a correction of 2 per cent for hydrogen would still leave a 3.6 per cent difference in favor of the copper oxide furnace. Such a difference would not be permissible. An explosion method neglecting the ethane present is certainly very inaccurate and even the explosions of pure oxygen with hydrogen and methane are not altogether satisfactory. Since approximately 10 cc. of the gas is used for the explosion, an error in reading of 0.1 cc. means 1.0 per cent; therefore a greater accuracy cannot be expected except by averaging a number of analyses.

Methane and Ethane, CH_4 and C_2H_6

Methane and ethane are always determined together either by explosion or by slow combustion with oxygen. Sometimes the determination of ethane in carburetted water gas and coal gas is neglected, which throws the results for hydrogen low and those for methane too high. Ethane is always present in these two gases and should be determined. Hydrogen must be removed before ethane can be computed if mixed with methane.

In the explosion method for methane and ethane, a volume of oxygen equal to from 4 to 5 times the volume of gas taken is added, and an electric spark passed through the mixture. The contraction is read, and the contraction after passing into potassium hydroxide is also noted. The methane and ethane are then computed by the following formulas:

$$\frac{2 \times \text{contraction} - \text{vol. of } CO_2}{3} = V = \text{Vol. of } CH_4 + C_2H_6.$$

$$\frac{CO_2}{V} = 1 \text{ to } 2.$$

If the number is 1 the gas is all methane and if it is 2 the gas is all ethane. If the number is 1.2 the gas is a mixture of methane and ethane, and the fraction indicates the amount of ethane present; thus $0.2 \times V =$ volume of ethane in the gas. If only a fraction of the total gas is used for explosion these results must be multiplied by the proportionality factor.

In the slow combustion method all of the gas remaining after the removal of hydrogen is passed into a combustion pipette (the Illinois apparatus uses only a fraction of the gas) containing a known amount of oxygen sufficient for combustion of the hydrocarbons. At the very inlet to the pipette is a platinum coil heated to a bright red heat. By passing the gas slowly over this hot platinum coil in the presence of oxygen complete combustion takes place. The contraction in volume is noted, also the amount of carbon dioxide absorbed in potassium hydroxide. By using the formulas given above, the percentage of methane and ethane is obtained.

Nitrogen, N_2

Nitrogen may be slightly oxidized by the electric spark and not at all by the platinum coil. Since nitrogen is inert to all the absorption and combustion methods used in technical gas analysis, it is always obtained by difference. A check on the nitrogen percentage may be made by passing 100 cc. of the gas over copper oxide at from 500 to 600 deg. C. into a potassium hydroxide pipette. In this way all the carbon dioxide, illuminants, carbon monoxide, hydrogen, methane, ethane, and practically all of the oxygen (by reaction with hydrogen, carbon monoxide, and the reduced copper oxide) are removed. This leaves only nitrogen and the zero group of gases.

TABLE 7

SUMMARY OF INFORMATION RELATING TO METHODS FOR GAS ANALYSIS

	Components	Gas vol. in cc. sol. in 1 cc. H_2O at 15° C.	Gas densities at 0° C. and 760 mm. Air = 1	B.t.u. per cu. ft. gross at 60° F. and 30 in. mercury	Methods	Apparatus	Remarks
1	CO_2	1.003	1.529		(a) 10% solution NaOH (b) 30-40% solution KOH	Flow type Ill. Gas App. Closed type Orsat	
2	C_2H_4	0.161	0.9729	1591.	(a) Saturated bromine water (b) Fuming sulphuric acid	Ill. Gas App. Orsat type	To avoid removal of C_6H_6 dilute by 1 of water to 2 of sat. bro.
3	C_6H_6	Vapor very slightly soluble		3634.	(a) Fuming sulphuric acid (b) Saturated bromine water	Osat type Ill. Gas App.	Nos. 2 and 3 usually determined together as illuminants
4	O_2	0.0341	1.1053		(a) Potass. pyrogallate, 20 of (1 H_2O:3 KOH) to 1 of pyrogallic acid (b) Phosphorus	Ill. Gas App. Either in Orsat	
5	CO	0.0254	0.9670	321.	(a) Acid cuprous chloride 200 g. to one l. conc. HCl sp. gr. 1.12 (b) Ammo. cuprous chloride 150 g. to one l. $H_2O + NH_3$ (or see p. 30)	Ill. Gas App.	For combustion, see p. 33 Use 2 pipettes with Orsat app.
6	H_2	0.0188	0.0696	326.	(a) Combustion with CuO at 300° C. (b) Explosion with O_2 (c) Palladinized asbestos	Ill. Gas App.	
7	CH_4	0.0369	0.5529	978.	(a) Slow combustion, Pt. spiral (b) Explosion with O_2, electric spark	Ill. Gas App.	
8	C_2H_6	0.0541	1.306	1689.	(a) Slow combustion, Pt. spiral (b) Explosion with O_2, electric spark	Ill. Gas App.	
9	N_2	0.0168	0.9673		(a) By difference		

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